CLAIMS

[Claim(s)]
[Claim 1]Resin coated steel for containers excellent in processability, adhesion, heat resistance, and corrosion resistance having the polyester resin coating whose plane orientation coefficient of the outermost layer of a coat thermal shrinkage stress in all the plane directions of a coat is below 30 gf(s)/mm^2, and is 0.02 or more in a steel sheet surface which turns into an inner surface of a container at least.
[Claim 2]To a steel sheet surface which heats a steel plate at 180-240 **, and turns into an inner surface of a container at least. Sticking-by-pressure lamination of the biaxially oriented polyester film whose plane orientation coefficient of a field which has thermal shrinkage stress below 300 gf(s)/mm^2 in all the plane directions, and serves as the after-covering outermost layer is 0.05 or more is carried out, A manufacturing method of resin coated steel for containers excellent in processability, adhesion, heat resistance, and corrosion resistance which are characterized by quenching below to a glass transition point of this polyester film within 20 seconds after sticking by pressure.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application]In this invention, it is related with a polyester resin coated steel sheet for containers, and a manufacturing method for the same.
Therefore, it is related with a polyester resin coated steel sheet suitable for the container material in which the processability in the can manufacturing process of the diaphragm redrawing can (DTR can) accompanied by a diaphragm can, a diaphragm redrawing can (DRD can), and stretch processing, etc., adhesion, heat resistance, and the corrosion resistance after canning are required more of details, and a manufacturing method for the same.

[0002]
[Description of the Prior Art]Conventionally, the diaphragm can was processed after giving paint of 1 time or multiple times, and baking to a tin sheet, an electrolysis chromate treatment steel plate, or an aluminum plate. Thus, not only a baking process is complicated, but painting needed great baking time. In order to discharge a lot of solvents at the time of coat formation, it had the fault that a discharge solvent had to be led to a special incinerator and had to be incinerated also from a public nuisance side.
[0003]In recent years, in order to solve these faults, the proposal of the thing which covered polyester film to the metal plate, and its manufacturing method is made.
[0004]As the example, the polyester film which has a crystal melting point of 210-250 ** is covered to a metal plate using a primer, The refractive index of the thickness direction of a coat by 1.5100-1.5600 And that whose refractive indicees within a field are 1.5900-1.6500 and its manufacturing method (JP,3-87249,A), Cover polyester film to a metal plate using a primer, and the X diffraction intensity ratio of the field (100) of a coat and a field (110) by 0.5-15 And the can using that whose anisotropy index of an in-plane orientation is 30 or less, and its cladding (JP,3-101930,A), A steel plate is covered with with the softening temperature of 170-235 **, and a crystal melting point of 190-250 ** polyester resin coating via direct or a primer, and a thing, a manufacturing method, etc. of the range of the orientation coefficients 0-0.100 of a coat (DE-3836858A1) are indicated.
[0005]
[Problem(s) to be Solved by the Invention]However, the average value to 5 micrometers of depth directions of the field which touches prism is acquired, and the refractive index which X diffraction intensity only shows the grade of crystallization of a coat, and is measured with an Abbe refractometer does not show the information on the whole coat. It can say that the same may be said of the plane orientation coefficient computed from the measured refractive index. About distortion or plasticity of a coat, it cannot be overemphasized that the information on the whole coat is required. For this reason, in the coated steel board which has the coat specified with these property values, sufficient processability may not be securable. Although the contraction or exfoliation by a heated atmosphere like for example, outside printing may occur in a can manufacturing process, in these property values, it is not practical.
[0006]This invention was made in view of the above-mentioned actual condition, and secures the

processability and adhesion of a coat, The resin coated steel for diaphragm cans which has the resin membrane structure which contraction or exfoliation of the resin membrane in the process of receiving heat, such as printing and repair coating baking, did not occur among the can manufacturing process, and had sufficient corrosion resistance over contents after canning is provided.

[0007]

[Means for Solving the Problem]The gist of this invention is as follows.

[0008]** a steel sheet surface which turns into an inner surface of a container at least -- thermal shrinkage stress in all the plane directions of a coat -- below 30 gf(s)/mm^2 -- and resin coated steel for containers excellent in processability, adhesion, heat resistance, and corrosion resistance having the polyester resin coating whose plane orientation coefficient of the outermost layer of a coat is 0.02 or more.

[0009]** To a steel sheet surface which heats a steel plate at 180-240 **, and turns into an inner surface of a container at least. Sticking-by-pressure lamination of the biaxially oriented polyester film whose plane orientation coefficient of a field which has thermal shrinkage stress below 300 gf(s)/mm^2 in all the plane directions, and serves as the after-covering outermost layer is 0.05 or more is carried out, A manufacturing method of resin coated steel for containers excellent in processability, adhesion, heat resistance, and corrosion resistance which are characterized by quenching below to a glass transition point of this polyester film within 20 seconds after sticking by pressure.

[0010]

[Function]This invention is covered by the steel sheet surface where the polyester resin film which has plane orientation nature serves as an inner surface of a can. It is resin coated steel which has in detail the polyester resin coating whose plane orientation coefficient of the outermost layer of a coat the thermal shrinkage stress in all the plane directions of a coat is below 30 gf(s)/mm^2, and is 0.02 or more in the steel sheet surface which turns into an inner surface of a container at least. Even if polyester resin is covered by the steel sheet surface via a primer, it does not interfere.

[0011]Hereafter, an operation of this invention is described.

[0012]Since the reason which limited the coat covered with this invention by the steel plate to polyester resin coating does not have an olefin smell like polyolefin resin, such as polyethylene and polypropylene, as a cardinal trait of polyester resin, the outstanding contents characteristic that flavor nature is good is mentioned.

[0013]The polyester resin used by this invention is saturated polyester resin which does not include a double bond in a film chain, and is a polymer of saturated polyvalent carboxylic acid and saturated polyhydric alcohol as everyone knows.

[0014]As saturated polyvalent carboxylic acid, terephthalic acid, phthalic acid, isophthalic acid, There is carboxylic acid, such as succinic acid, azelaic acid, adipic acid, sebacic acid, dodecane dione acid, diphenylcarboxylic acid, 2, 6 naphthalene dicarboxylic acid, 1, 4 cyclohexanedicarboxylic acid, and anhydrous TORIMERRITO acid. As saturated polyhydric alcohol, ethylene glycol, 4 butanediol, 1, 5 pentanediol, 1, 6 hexandiol, propylene glycol, There are polytetramethylene glycol, a trimethylene glycol, triethylene glycol, neopentyl glycol, 1, 4 cyclohexane dimethanol, trimethylolpropane, pentaerythritol, etc. The simple substance and the blended polyester resin of the homopolymer which consists of these saturated polyvalent carboxylic acid and saturated polyhydric alcohol, and a copolymer are used.

[0015]What added the polyalkylene glycol derivative etc. can be used for the above-mentioned polyester resin for the purpose of the improvement of impact strength, retort nature, etc. Adding an antioxidant, a thermostabilizer, an ultraviolet ray absorbent, a spray for preventing static electricity, colorant, etc. if needed does not interfere.

[0016]In order to extract the steel plate covered with above-mentioned polyester resin coating, to apply to a can use and to secure the corrosion resistance after contents restoration especially, it is necessary to make the physical structure of the covered polyester resin coating into an orientation crystal structure.

[0017]Let thickness of the polyester film used for this invention be the range of 5-50 micrometers. In order to secure sufficient contents preservability supposing corrosion-resistant degradation by the film damage in a can manufacturing process, less than 5 micrometers is insufficient. On the other hand,

even if it exceeds 50 micrometers of a maximum, the effect in a corrosion-resistant point is saturated and becomes disadvantageous economically. Therefore, the film thickness made to laminate needs to be 5-50 micrometers, and let it be the range of 10-30 micrometers still more desirably.

[0018]In order according to this invention person's etc. knowledge to have sufficient processability and to secure the heat resistance after processing, and the corrosion resistance after contents restoration, sufficient adhesion power of specifying the plane orientation coefficient of the thermal shrinkage stress of polyester resin coating and the outermost layer of a coat, and a coat and a steel plate is needed.

[0019]It needs that the thermal shrinkage stress of all those plane directions is below 30 gf(s)/mm^2, and the plane orientation coefficient of the outermost layer of a coat is 0.02 or more as the characteristic of the laminated polyester resin coating. If this condition is satisfied, it will become possible to obtain the product which has sufficient processability and secures the heat resistance after processing, and the corrosion resistance after contents restoration.

[0020]The thermal shrinkage stress of the film in this invention and a coat means the maximum stress in initial tension 0gf/mm^2 measured using the apparatus for thermomechanical analysis (TMA-SS5000, the product made from SEIKO Electronic industry, a quartz probe), the heating rate of 10 ** / min, and 30-260 ** of time base ranges. About the thermal shrinkage stress of a coat, the obtained polyester resin coated steel sheet is immersed in chloride, a steel sheet surface is dissolved chemically, and it measures by exfoliating only polyester resin covering.

[0021]In this invention, the reason which limited the thermal shrinkage stress in all the plane directions of the polyester resin coating of the side used as a container internal surface to below 30 gf(s)/mm^2 is explained. The resin membrane of laminated steel produces distortion by processing, and thermal shrinkage stress increases. When processing is severe, the coat cannot finish bearing distortion, is fractured or produces a coat defect. When heated, a coat becomes easy to produce contraction. If the laminated steel which has the polyester resin coating which made the thermal shrinkage stress in all the plane directions of the coat before processing below 30 gf(s)/mm^2 as a result of examining this is used, A coat can be followed in footsteps also to a severe machining purpose like a DTR can, and there is little increase of the thermal shrinkage stress of the coat after processing, and it is hard to produce contraction of the coat in heating after processing.

[0022]The plane orientation coefficient of the outermost layer of the coat in this invention is computed by several 1 using an Abbe refractometer from the refractive index value for all directions of a coat where the light source measured sodium/D line by a 20 ** measuring condition, and middle liquid measured methylene iodide and temperature.

[0023]

[Equation 1]Plane-orientation-coefficient =(Nx+Ny)/2-NzNx: The refractive index of the thickness direction of the refractive-index Nz:polyester coat of the transverse direction of the refractive-index Ny:polyester coat of the lengthwise direction of a polyester coat [0024]A coat dissolves a steel plate chemically like the case of thermal shrinkage stress, and a surface is stuck through prism and it measures it.

[0025]In this invention, the reason for having made the plane orientation coefficient of the outermost layer of a coat or more into 0.02 is explained. In less than 0.02, barrier property [as opposed to the contents of polyester resin itself in a plane orientation coefficient] is remarkably inferior, and to strong corrosive contents, if saved for a long time [after-restoration], a steel plate will be corroded. Making the plane orientation coefficient of the outermost layer or more into 0.02 limited to the outermost layer, and it is because it is enabled to be able to secure the stability to hot water, namely, to prevent crystallization and hydrolysis by retorting.

[0026]The steel plate used by this invention is the plating steel plate and electrolysis chromate treatment steel plate of Sn plating, nickel plating, and Sn/nickel plating which performed chemical conversion to the upper layer of the plating layer, respectively. An electrolysis chromate treatment steel plate is a chromium chromate treatment steel plate currently called the common name TFS (TinFree Steel), and a chromium metal is [30-150mg/m^2 and hydration chrome oxide of coating weight] 5-20-mg/m^2 in chromium metal conversion. The chemical conversion performed to the upper layer of

each plating coat of Sn plating steel plate, a Sn/nickel plating steel plate, and nickel plating steel plate is chromium like TFS mentioned above, chromate treatment, chromate treatment called the CDC processing used as chemical conversion of a tin plate from the former, etc.
[0027]Of a container, since processing of a diaphragm etc. is performed, the adhesion of a steel plate and a coat is required. For this reason, the chemical conversion of a steel plate becomes important. About the adhesion of the steel plate of the laminated steel for diaphragm cans, and a lamination coat, when the adhesion power in a laminated steel state is measured by the peel method, the level stuck so firmly that the fracture of a coat takes place and peel strength cannot be measured is required at least. Since the breaking strength in a 12-micrometer PET film is 2.1 kg/10 mm about, the adhesion power beyond this is needed.
[0028]The peel methods are 10 mm in width, and 180-degree peel exfoliation, measure hauling speed on condition of 100 mm/min, and the preparation method of a sample, From the reverse field where the coat which is going to measure adhesion power with a steel plate was laminated, a cut is put only into a steel plate, only a steel plate is cut, without attaching a crack to the coat which it is going to measure, and it is considered as a sample.
[0029]If laminated steel which produces a film fracture in a peel strength measurement test also receives draw forming by a can manufacturing process, the adhesion power of a coat will decline. When processing is severe, a coat may exfoliate easily. 10 mm is required for the peel strength value of the coat after performing three-step draw forming practically on the conditions shown in Table 1 in 0.1kg /or more.
[0030]
[Table 1]

Ⅰ．第１段絞り
ブランク径：１８７mm 絞り比：１．５５
ＩＩ．再絞り
第一次再絞り比：１．３８ 第二次再絞り比：１．２６ 再絞り工程のダイスのコーナー部の曲率半径：０．４mm 再絞り工程のしわ押さえ荷重：４０００ｋｇ
ＩＩＩ．缶胴部の平均薄肉化率
成形前のポリエステル樹脂被覆鋼板の厚さに対して：２０％

[0031]Next, the manufacturing method of the resin coated steel of this invention is described. [0032]In this invention, heat adhesion method, i.e., the method of laminating by sticking polyester film to the heated steel plate by pressure, is adopted as a means to cover a polyester resin film to a steel plate.
[0033]The method of letting the inside of the heated furnace pass as a heating method of a board, the energizing heating method energized and heated to a steel plate, the induction-heating method, the method of contacting on the heated roll and heating, etc. are employable.
[0034]Container material receives severe processing in a can manufacturing process. For this reason, when manufacturing the laminated steel which covered polyester resin, sufficient adhesion power of polyester resin coating and a steel plate must be secured. In order to secure the adhesion power of polyester and a steel plate, it is necessary to make a steel plate and polyester of an adhesion interface amorphous. In order to secure the corrosion resistance after becoming a can, it is necessary to use an orientation crystal structure as the coat which it left to the outermost layer like the above-mentioned.
[0035]In order to make the polyester coat which made the adhesion interface with a steel plate

amorphous with heat adhesion method, and left the orientation crystal layer to the outermost layer, it is necessary to specify lamination conditions, such as the highest arrival temperature of a steel plate, time to cooling, and cooling temperature. That is, as lamination conditions, the steel plate temperature at the time of sticking by pressure shall be 180-240 **, and it needs to quench below to the glass transition point of this polyester film within 20 seconds after sticking by pressure.

[0036]Resin causes stress relaxation by heat and time, and, as for the resin which has an orientation crystal structure, the orientation crystal of resin is destroyed by heating. Also in the polyester film used for a lamination, stress relaxation and the fall of orientation crystallinity are caused with the heat at the time of a lamination. Therefore, below 30 gf(s)/mm^2 carries out the thermal shrinkage stress of all the plane directions of the polyester coat manufactured by lamination, And in order to make the plane orientation coefficient of the outermost layer of a coat or more into 0.02, it is necessary to combine above-mentioned lamination conditions and specific polyester film. It is necessary to use the biaxially oriented film whose plane orientation coefficient which has thermal shrinkage stress below 300 gf(s)/mm^2 in all the plane directions, and serves as the after-covering outermost layer is 0.05 or more as polyester film to be used.

[0037]At less than 180 **, polyester resin does not fully fuse, the steel plate temperature at the time of sticking by pressure does not become amorphous [resin of an adhesion interface with a steel plate], and sufficient adhesion power with a steel plate cannot be secured. On the other hand, the orientation crystal of polyester resin is thoroughly destroyed at more than 240 ** by the heat supplied from a steel plate. It may be 200-230 ** preferably.

[0038]If it does not quench below to an after-lamination glass transition point, resin of the steel plate interface fused with heating of the lamination recrystallizes quenching below to the glass transition point of this polyester film within 20 seconds, after covering a coat to a steel plate, it serves as a non-orientation crystal, imitates the fall of adhesion, and is for **.

When it has been after-lamination more than 20 seconds, it is because all the orientation crystals of a coat are destroyed by the heat from a steel plate.

Preferably, cooling is started within 10 seconds after sticking by pressure.

[0039]although the method which is immersed in water and quenched as the method of quenching, the method of spraying and quenching the cold air, the methods of blowing air and water simultaneously and quenching them, these concomitant use, etc. are employable, carry out for adopting which method -- it is necessary to fully secure a cooling rate

[0040]When the maximum of the thermal shrinkage stress of a plane direction uses the film which exceeds 300 gf(s)/mm^2 as polyester film, It is difficult for below 30 gf(s)/mm^2 to carry out the thermal shrinkage stress of all the plane directions of the polyester coat manufactured in the method of making the above-mentioned laminating method, i.e., the steel plate temperature at the time of sticking by pressure, 180-240 **, and quenching below to the glass transition point of this polyester film within 20 seconds after sticking by pressure. For this reason, the thermal shrinkage stress in all the plane directions of the polyester film to be used was limited to below 300 gf(s)/mm^2.

[0041]Also when the biaxially oriented film whose plane orientation coefficient of the field used as the after-covering outermost layer is less than 0.05 is used, it is difficult to make the plane orientation coefficient of the outermost layer of a coat or more into 0.02 in the above-mentioned laminating method. For this reason, the plane orientation coefficient of the field used as the after-covering outermost layer of the polyester film to be used was limited or more with 0.05.

[0042]

[Example]After bonding a biaxial-stretching polyester resin film to both sides of TFS (0.20 mm of board thickness, temper DR9, and 80 mg of chromium metal/m^2, hydration chrome oxide 15mg/m^2) heated by the energizing heating method by thermo-compression, resin coated steel was obtained with the heat adhesion method which carries out water quenching. The various characteristics of film A-D used for the example were shown in Table 2, and the various characteristics of lamination conditions and a lamination coat were shown in Tables 3-6. The film used the monolayer type thing and the two-layer type thing by co-extrusion. What "-" in front did not evaluate the item for is shown.

[0043]

[Table 2]

使用フィルム

No.	A	B	C	D	E	F
タイプ	単層	単層	単層	二層	二層	二層
厚み	30μ	30μ	30μ	25μ	25μ	25μ
Tm 非接着層	229℃	230℃	228℃	242℃	242℃	240℃
Tm 接着層				233℃	232℃	231℃
Tg 非接着層	69℃	68℃	67℃	74℃	73℃	75℃
Tg 接着層				75℃	74℃	73℃
熱収縮応力（面方向最大値）〔gf／mm²〕	180	350	190	250	400	260
被覆後最表層となる面の面配向係数	0.0824	0.0756	0.0291	0.1205	0.1035	0.0354

[0044]
[Table 3]

ラミネート条件および皮膜の特性

	実施例1		実施例2		実施例3	
	内面	外面	内面	外面	内面	外面
使用フィルム	A	A	D	D	A	D
ラミネート温度	215℃	215℃	225℃	225℃	220℃	220℃
冷却開始までの時間	3秒	3秒	5秒	5秒	8秒	8秒
冷却温度	50℃	50℃	60℃	60℃	55℃	55℃
皮膜の熱収縮応力（面方向最大値）〔gf／mm^2〕	10.5	10.7	16.3	16.2	8.3	18.0
皮膜の面配向係数	0.0449	0.0450	0.0765	0.0765	0.0414	0.0795
ラミネート皮膜外観	○	○	○	○	○	○
密着性	○	○	○	○	○	○
成形加工性	○	○	○	○	○	○
耐熱性	○	○	○	○	○	○
耐熱水性	○	○	○	○	○	○
耐食性	○	○	○	○	○	○

[0045]
[Table 4]

ラミネート条件および皮膜の特性

	実施例4		比較例1		比較例2	
	内面	外面	内面	外面	内面	外面
使用フィルム	D	A	F	B	E	C
ラミネート温度	222℃	222℃	222℃	222℃	185℃	185℃
冷却開始までの時間	2秒	2秒	2秒	2秒	2秒	2秒
冷却温度	45℃	45℃	45℃	45℃	45℃	45℃
皮膜の熱収縮応力（面方向最大値）〔gf／mm^2〕	16.9	8.0	18.5	34.4	50.2	15.8
皮膜の面配向係数	0.0807	0.0415	0.0021	0.0346	0.0810	0.0066
ラミネート皮膜外観	○	○	○	○	○	○
密着性	○	○	○	○	×	×
成形加工性	○	○	×	×	−	−
耐熱性	○	○	−	−	−	−
耐熱水性	○	○	−	−	−	−
耐食性	○	○	−	−	−	−

[0046]
[Table 5]

ラミネート条件および皮膜の特性

	比較例3		比較例4		比較例5	
	内面	外面	内面	外面	内面	外面
使用フィルム	E	B	D	A	D	A
ラミネート温度	240℃	240℃	250℃	250℃	170℃	170℃
冷却開始までの時間	2秒	2秒	2秒	2秒	2秒	2秒
冷却温度	45℃	45℃	45℃	45℃	45℃	45℃
皮膜の熱収縮応力（面方向最大値）〔gf／mm^2〕	65	45	6.5	3.2	31	17.4
皮膜の面配向係数	0.0185	0.0109	0.0105	0.0094	0.0795	0.0414
ラミネート皮膜外観	○	○	○	○	○	○
密着性	○	○	○	○	×	×
成形加工性	×	×	△	△	×	×
耐熱性	−	−	△	△	−	−
耐熱水性	−	−	×	×	−	−
耐食性	−	−	×	×	−	−

[0047]
[Table 6]

ラミネート条件および皮膜の特性

	比較例6		比較例7	
	内面	外面	内面	外面
使用フィルム	D	A	D	A
ラミネート温度	222℃	222℃	222℃	222℃
冷却開始までの時間	2秒	2秒	25秒	25秒
冷却温度	80℃	80℃	45℃	45℃
皮膜の熱収縮応力（面方向最大値）〔gf／mm^2〕	16.2	7.4	6.5	5.5
皮膜の面配向係数	0.0790	0.0408	0.0174	0.0158
ラミネート皮膜外観	○	○	○	○
密着性	×	×	○	○
成形加工性	×	×	○	○
耐熱性	−	−	−	−
耐熱水性	−	−	−	−
耐食性	−	−	−	−

[0048](1) O and x estimated the appearance of the laminated steel which was obtained as for the outside view.
[0049](2) The adhesion peel test was done and O and the thing which was not carried out were evaluated for what carried out the film tear as x. Peel test conditions are 10 mm in width, an angle of 180 degrees, and hauling speed 100 mm/min.
[0050](3) Molding workability shaping was performed on the conditions shown in Table 7.
[0051]
[Table 7]

〔成形条件〕

Ⅰ．第１段絞り
ブランク径：１８７mm 絞り比：１．５５
ＩＩ．再絞り
第一次再絞り比：１．３８ 第二次再絞り比：１．２６ 再絞り工程のダイスのコーナー部の曲率半径：０．４mm 再絞り工程のしわ押さえ荷重：４０００ｋｇ
ＩＩＩ．缶胴部の平均薄肉化率
成形前のポリエステル樹脂被覆鋼板の厚さに対して：２０％

[0052]The above shaping was performed and it evaluated as the following.
[0053]The case where a coat did not exfoliate the case where a coat exfoliates the case where a coat exfoliates the case where a coat exfoliates the case where a coat exfoliates in the 1st step diaphragm, in xx and the first redrawing, in x and the second redrawing, in ** and the second redrawing, to ** and the second redrawing was made into O.
[0054](4) After heat-treating at the temperature supposing baking of outside printing of the heat-resistant profitable **** last redrawing can, i.e., 200 **, for 5 minutes, discoloration of the polyester resin coating of a can body, the crack, and the exfoliation situation were observed with the naked eye.
[0055](5) The hot-water-resistance profitable **** last redrawing can was put into the retort pot, a 120 ** steam performed hot water processing for 30 minutes, the exfoliation situation of the polyester coat was observed with the naked eye, and the situation of exfoliation was divided into the three-stage of O, **, and x, and was evaluated.
[0056](6) The corrosion-resistant profitable **** last redrawing can was filled up with acetic acid water 3%, it opened after three-month storage at 50 **, and the corrosion situation of can internal was observed with the naked eye, and the situation of corrosion was divided into the three-stage of O, **, and x, and was evaluated.
[0057]
[Effect of the Invention]The resin coated steel of this invention can manufacture cheaply the diaphragm can which was excellent in the heat resistance in a can manufacturing process and in which the corrosion resistance after canning was excellent. It can be widely used also as a charge of other can top [not only a diaphragm can but], easy open lid, 5gal can, and container material.

[Translation done.]